ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PHENACYL ETHYL CARBAZOLIUM SALT AS A LONG WAVELENGTH PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FENAÇİLETİL KARBAZOLYUM TUZU KULLANILARAK UZUN DALGABOYUNDA SERBEST RADİKAL FOTOPOLİMERİZASYONU

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Merve Kara, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 509141020, successfully defended the thesis entitled "PHENACYL ETHYL CARBAZOLIUM SALT AS A LONG WAVELENGTH PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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Merve KARA
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ABBREVIATIONS

CV	**:** Cyclic voltammetry
$CDCl_3$	**:** Deuterated chloroform
DSC	**:** Differential scanning calorimetry
DMPA	**:** 2,2-dimethoxy-2-phenylacetophenone
EC	**:** 9-Ethylcarbazole
EGDMA	**:** Ethylene glycol dimethacrylate
FT-IR	**:** Fourier transform infrared resonance spectroscopy
GPC	**:** Gel permation chromatography
^{1}H NMR	**:** Hydrogen nuclear magnetic resonance spectroscopy
ISC	**:** Inter system crossing
$KSbF_6$	**:** Potassium hexafluoroantimonate(V)
MA	**:** Methyl acrylate
MMA	**:** Methyl methacrylate
NVC	**:** *N*-vinylcarbazole
PECH	**:** Phenacyl ethyl carbazolium hexafluoroantimonate
PI	: Photoinitiator
St	**:** Styrene
THF	**:** Tetrahydrofuran
UV	**:** Ultraviolet

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PHENACYL ETHYL CARBAZOLIUM SALT AS A LONG WAVELENGTH PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION

SUMMARY

Photoinitiated polymerization, or briefly photopolymerization, is usually described as a typical process that transforms functional monomers, oligomers, and polymers into higher molecular weight polymers by a chain reaction under exposure of light. The reaction was initiated by reactive species (free radicals or ions), which are generated from photo-sensitive compounds, in particular photoinitiators and/or photosensitizers, by UV-Vis light irradiation.

In recent years, there has been a growing interest in the photoinduced polymerizations of many different types of monomers and oligomers. Many olefinic and acrylic monomers are readily polymerizable by a free radical mechanism, while other compounds such as epoxides and vinyl ethers are solely polymerizable by a cationic mechanism. Notably, initiation techniques based on photoinduced process have several advantages over conventional heat-induced techniques. The most striking one is that polymerizations can be started at low temperatures, and thermally stable initiators can be employed. It also offers lower energy cost, and solvent-free formulation, thus elimination of air and water pollution. Generally, the photoinitiated polymerization system is composed of suitable monomers such as acrylates or epoxides and a highly photosensitive photoinitiator. Upon UV irradiation, the photoinitiator decomposes with a high quantum yield and produces active species that initiate polymerization. Photoinitiated polymerization has now found many applications in areas such as adhesives, nonstick release coatings, and abrasion resistant coatings for plastics, optical fiber coatings, reinforced composites, stereolithography, holography, optical waveguides, graphic arts, printing plates, dental fillings, and microelectronics.

Since the photoinitiator is one of the most important part of a UV initiated polymerization, many research effords have been devoted to understand what type of photoinitiators is applicable to generate free radicals or ions. There has been great effort to develop photoinitiators with enhanced absorption characteristics, solubility, low odor, low migration, and non-yellowing properties. In particular, the improvement of photoinitiators absorbing light in the near UV-visible light range of the electromagnetic spectra is a key challenge in the last decade due to the fulfillment of green chemistry demands.

Phenacyl type photoinitiators containing sulphonium, phosphonium, ammonium, and pyridinium ions are capable for the polymerization of both cationically and free radically polymerizable monomers such as oxiranes, vinyl ethers, (meth)acrylates, and styrenes. The initiation is accomplished by direct or indirect (sensitized) photolysis of the salts. Depending on the type of the salt, the photoinitiation step

involves reversible or irreversible processes. The photolysis of phencyl sulphonium compounds proceeds by a reversible process, while the other types, phenacyl ammonium or phosphonium salts, undergo irreversible photolysis leading to complete fragmentation of the photoinitiator.

In the current thesis, a new phenacyl-type photoinitiator based on ethyl carbazole as a long wavelength photoinitiator is developed for free radical polymerization. Phenacyl ethyl carbazolium hexafluoroantimonate (PECH) photoinitiator was synthesized in a two-step, one-pot manner by quaternizing ethyl carbazole with phenacyl bromide and subsequent ion exchange reaction with potassium hexafluoroantimonate. Under irradiation, PECH tends to undergo homolytic bond cleavage bringing about initiating free radicals. Optical behavior of the photoinitiator was carefully evaluated and free radical photopolymerization of a series of vinyl monomers including methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), and *N*-vinylcarbazole (NVC) has been successfully achieved under UV light irradiation. However, as evidenced by cyclic voltammetry and real-time photobleaching studies, formation of initiating cationic species is highly unlikely as the photochemically formed charged carbazole units tend to couple.

FENAÇİLETİL KARBAZOLYUM TUZU KULLANILARAK UZUN DALGABOYUNDA SERBEST RADİKAL FOTOPOLİMERİZASYON

ÖZET

Polimerizasyon; monomer adı verilen çok sayıda molekülün bir seri kimyasal reaksiyonla birleşerek bir makromolekül oluşturmasıdır. Kısacası monomerlerin polimerlere dönüşmesine polimerizasyon denir. Polimerizasyon süreci birbirini izleyen aktivasyon, başlama, ilerleme, bitiş olmak üzere 4 safhadan oluşur. Aktivasyon Safhası: Polimerizasyonu başlatmak için reaktif türler oluşması gerekmektedir. Serbest radikaller oldukça zayıf bir bağ içeren başlatıcıların çeşitli aktivatörler (ısı, kimyasal bileşikler, ışık) vasıtası ile parçalanmasıyla oluşur. Işık uygulama yönteminde aktivatör olarak ultraviyole ya da görünür ışık kullanılmaktadır. Başlama Safhası: Polimerizasyon, aktivasyon sonucu oluşan serbest radikalin monomer ile reaksiyona girmesi ile başlar. Serbest radikaller çift bağ içeren monomere saldırarak tekrar reaktif gruplar oluştururlar. İlerleme Safhası: Oluşan reaktif gruplar başka monomerlere bağlanarak yeni bir reaktif grup oluştururlar. Böylece bütün moleküller birbirlerine bağlanarak zincirin büyümesine yol açarlar. Bitiş Safhası: İlerleme reaksiyonunun kitle içindeki monomer molekülleri bitinceye kadar devam etmesi beklenir. Ancak pratikte, polimer zincirinin bitimine neden olan diğer reaksiyonlar ilave reaksiyonu engelleyebilir. Bu reaksiyonlar ölü polimer zincirleri oluştururlar. İlave reaksiyona uğramazlar. Polimerizasyon sonunda elde edilen polimerin, fiziksel özellikleri üzerinde, moleküler ağırlığının, çapraz bağların ve zincir dallanmasının etkisi büyüktür.

Işıkla başlatılan polimerizasyon veya fotobaşlatılmış polimerizasyon, mor ötesi-görünür bölgedeki ışık altında fotobaşlatıcı ve/veya fotouyarıcı gibi ışığa duyarlı bileşiklerden üretilen reaktif türler (serbest radikaller veya iyonlar) vasıtasıyla başlatılan zincir reaksiyonu sonucu monomerin polimere dönüştürüldüğü bir süreç olarak tanımlanır.

Son yıllarda, fotobaşlatılmış polimerizasyon sahip olduğu üstün özellikleri sebebiyle ve pek çok ekonomik, ekolojik beklentiyi biraraya getirdiği için hayli ilgi çekmektedir. Sahip olduğu mükemmel avantajları dolayısı ile kaplama, mürekkep, baskı levhaları, yapıştırıcı, vernik, elektronik malzemeler, fotolitografi, boya, optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamda polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır.

Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilmektedir. Ancak, çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından serbest radikal ve katyonik sistemlere daha fazla ilgi duyulmaktadır. Genellikle endüstriyel uygulamalarda serbest radikal fotopolimerizasyon sistemleri kullanılmaktadır. Fakat, bu tip polimerizasyonların oksijenin yavaşlatma etkisi ve son ürünün özelliklerini etkileyebilen kürleşme

sonrasındaki kısıtlamalar gibi bazı dezavantajları bulunmaktadır. Bu nedenle, fotobaşlatılmış katyonik polimerizasyon özellikle bu dezavantajların giderilmesi açısından gelecekte daha fazla yer alacağı da düşünülmektedir.

Fotopolimerizasyon yönteminin en önemli bileşenleri başlatıcılardır. Bu sebeple birçok araştırmacı bu alanda yeni yöntemler geliştirmeye çalışmaktadır. Monomer ve başlatıcı arasındaki yapısal uyumluluk, polimerizasyonun ilerleyişi açısından önem kazanmaktadır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan radikaller tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken çok fonksiyonlu monomerlerde ise çapraz bağlı yapılara dönüştürülmesini sağlar. Polimerik fotobaşlatıcılar çapraz bağlanacak filmin içinde göç edememe ve kolay sentezlenebilme gibi avantajlar taşımaktadır. Buna ilave olarak, fotopolimerizasyon sonucu oluşan ürünlerin küçük moleküllü yapılar olması nedeniyle sağlığa zarar verilmesi engellenmiş olur ve polimer üzerinde çok sayıda fotoaktif grupların bulunması çapraz bağlanma süresince belirgin üstünlükler sağlar. Uygun ışık şiddeti kullanılarak başlatıcı konsantrasyonu ve polimer zincirlerinin boyu ayarlanabilir. Polimerlerin ışığı absorplamasıyla fiziksel ve kimyasal özelliklerinde değişmeler gerçekleşir. Görünür bölgede absorbansa sahip başlatıcılar çok ilgi çekicidir, zira diş dolgu malzemelerinde, fotorezistlerde, matbaacılıkta, entegre devrelerde, lazer ile uyarılmış üç boyutlu kaplamalarda, halografik kayıtlarda ve nano boyutlu mikromekaniklerde kullanılmaktadır.

Fotokimyasal başlatıcının etkinliğini arttırıcı çalışmalar, monomer sistemlerdeki değişikliklerin daha pahalı olması nedeniyle önem kazanmaktadır. Bir fotokimyasal başlatıcının aşağıdaki özelliklere sahip olması beklenir:

a) Başlatıcının 300-400 nm civarında kuvvetli bir ışık absorbsiyonuna sahip olması. (Kullanılan ticari ışık kaynaklarının bir çoğu bu dalga boylarında ışık yayımlamaktadır.)
b) Işığın absorblanması sonucunda oluşan reaktif merkezlerin (genellikle radikallerin) monomerlerle etkin bir şekilde reaksiyona girebilmesi.
c) Çözünürlük.
d) Isısal kararlılıkla formüle edilmiş sistemlerin uzun süre dayanıklılığının sağlanması.
e) Elde edilen polimere renk ve koku vermemesi.
f) Başlatıcının ve aydınlatma sonucu oluşan ürünlerin toksik olmaması.

Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre *Tip I* ve *Tip II* fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır:

Tip I fotobaşlatıcılar, radikal vermek üzere doğrudan foto parçalanmaya uğrayan, çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşikleridir. *Tip II* başlatıcılarda, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken, etkin olmayan ketil radikalleri birbirleriyle kenetlenerek başlatıcı reaktif olarak davranmazlar. Radikal üretimi iki molekülün etkileşimi sonucu olan, *Tip II* fotobaşlatıcılar, tek molekülün parçalanarak radikal oluşturduğu *Tip I* fotobaşlatıcılara göre daha yavaş çalışmaktadır. Diğer yandan, *Tip II* fotobaşlatıcılar daha iyi optik özelliklere sahip olduklarından, düşük enerjili ışık kaynaklarıyla çalışma imkanı sunmaktadırlar. Ayrıca, *Tip I* fotobaşlatıcılar ile elde edilen polimerler, ışığa mağruz kaldıklarında α-bölünme mekanizması sonucu, uçucu yan ürünler meydana getirirler. Oluşan bu ürünler kötü kokuya neden olur. Bu

açıdan bakıldığında, *Tip II* fotobaşlatıcılarda ki ketil radikali tekrar ketona yükseltgenebildigi gibi birleşerek yüksek molekül ağırlıklı ve daha az uçucu bileşikler oluşturarak hedef ürünlerden uzaklaşırlar. Bu üstün özelliğinden dolayı, *Tip II* fotobaşlatıcılar daha çok tercih edilir. Etkili bir başlatma olabilmesi için, hidrojen koparma reaksiyonu diğer yan reaksiyonlarla (uyarılmış fotobaşlatıcıların enerjilerini oksijen ya da monomere aktarmasıyla enerjinin boşa harcanması) yarışabilmelidir. Bu sebepten dolayı *Tip II* serbest radikal fotopolimerizasyonu oksijene karşı yüksek seviyede duyarlıdır. Hidrojen verici grupların seçimi bu sistemde büyük önem kazanmıştır. *Tip II* fotobaşlatıcılarda, hidrojen verici moleküller olarak kullanılan amin, eter, alkol ve tiyol molekülleri arasında tersiyer aminler en çok tercih edilenlerdir. Ancak tersiyer aminlerin kötü kokulu, zehirli, kolay uçucu olması, göçme gibi olumsuz yönleri vardır.

Bu çalışmada, teknolojik ve bilimsel uygulamalara yönelik olarak konjuge etil karbazol ihtiva eden yeni bir fenaçil tipi fotobaşlatıcı tasarlanmış, sentezi, karakterizasyonu yapılmış ve radikalik polimerizasyon için başlatma etkinliği incelenmiştir. Fenaçil etil karbazolyum hekzafloroantimonat fotobaşlatıcısının sentezi iki adımda gerçekleştirilmiştir. Öncelikle 2-bütanon içerisinde çözünmüş olan etil karbazol, fenaçil bromür ilavesi ile kuaternize edilmiştir ve ardından ikinci adımda potasyum hekzafloroantimonat eklenerek iyon değişim reaksiyonu gerçekleştirilmiştir. Sentezlenen fotobaşlatıcının karakterizasyonu ^{1}H NMR ve diğer spektroskopik analiz yöntemleriyle yapılmış ve ardından bir takım vinil monomerleri için radikalik fotobaşlatılmış polimerizasyon denemleri yapılmıştır.

Bu fenaçil tipi fotobaşlatıcı, UV ışığın göreceli olarak daha yüksek dalga boylarındaki ışımaları absorbe etmektedir. Bu özellik fenaçil etil karbazolyum hekzafloroantimonat fotobaşlatıcısını diğer fenaçil türü fotobaşlatıılardan önemli kılmaktadır. Aydınlatma ile birlikte elde edilen bu tuzda homolitik bağ kırılması meydana gelmesi sonucu başlatma etkinliğine sahip olan serbest radikaller oluşmakta ve böylece üretilen bu reaktif türler yardımıyla polimerleşme reaksiyonları gerçekleşmektedir. Metil metakrilat, metil akrilat, stiren ve *N*-vinilkarbazol dahil olmak üzere bir dizi vinil monomerlerin serbest radikal fotopolimerizasyonu 350 nm'de başarılı bir şekilde bu yeni foto başlatıcı kullanılarak yapılmıştır. Ancak, halkalı ve vinil eterler dahil olmak üzere monomerlerin katyonik fotopolimerizasyonu başarısız olmuştur. Bununla ilgili daha ileri çalışmalar devam etmekte olup ayrıca başka bir çalışma olarak incelenecektir.

1. INTRODUCTION

The discovery and development of onium salt photoinitiators has resulted in numerous advancements in the area of photopolymerization techniques [1-4]. Iodonium [5], sulfonium [5-7], phosphonium [8, 9], and pyridinium [10, 11] salts are among the most extensively used onium salts. They have found use in many diverse areas of coatings, adhesives, printing inks, stereolithography, holographic recording, photocurable composites, and microelectronic photoresists etc. Phenacyl onium salts are of particular interest.

They are synthesized by the reaction of phenacyl halide compounds with the corresponding heteroatom containing nucleophiles followed by an anion exchange process with potassium or sodium salts containing non-nucleophlic counteranions [12]. These compounds are highly photosensitive and their photolysis mechanism generally involves homolytic and/or heterolytic bond cleavage upon irradiation giving rise to the formation of radical or cationic species. In addition, an electron transfer of the radical species resulted in homolytic bond cleavage can also contribute to the formation of cationic species.

The general photolysis mechanism of an anilinium salt as a typical example of phenacyl-based photoinitiator is shown in Figure 1.1. Given the formation of both radical and cationic species, the initiation of corresponding free radical and cationic polymerizations can be successfully achieved by these photoinitiators. Several phenacyl-type photoinitiating systems have been designed and utilized for free radical and/or cationic photopolymerizations [13-21]. In a recent study, phenacyl pyridinium salt macrophotoinitiators based on polystyrene-*b*-poly(2-vinyl pyridine) were used as efficient means for photo-switching the behavior of block copolymers from cationic to neutral states while initiating free radical and cationic photopolymerizations [22].

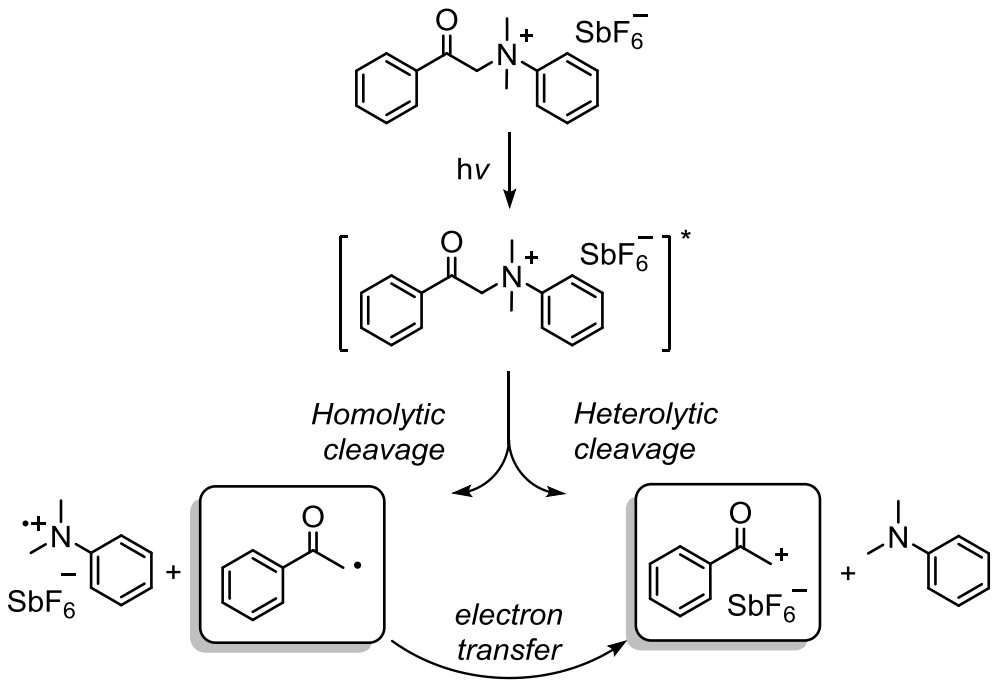


Figure 1.1 : Photolysis of phenacyl anilinium salt.

Spectral sensitivity of phenacyl onium salts lies mainly at UV regions around or below 300 nm which necessitates using high-energy lightning sources to achieve successful photolysis. In order to increase their optical absorption characteristics to higher wavelengths several approaches have been undertaken. Highly conjugated compounds, for example, are used to form phenacyl-based photoinitiators that absorb light at higher wavelengths due to the extended conjugation. Crivello and Kong reported the synthesis of a series of phenacylsulfonium salts containing modified polynuclear functional groups [23]. Incorporating conjugated groups extended the absorption characteristics of the photoinitiators. However, in some cases, photoinitiation efficiency was found to decrease probably due to the rapid fluorescence decay of the excited singlet state.

Another approach concerns photosensitization using various photosensitizers. Most often active at visible light regions, these photosensitizers are capable of interacting with photoinitiators in the excited state sensitizing photoinitiators to induce their photolysis. An electron transfer between the singlet or triplet excited state photosensitizers and phenacyl photoinitiator has been suggested in this respect. Polynuclear aromatic compounds including anthracene, perylene, and phenothiazine have been reported as efficient photosensitizers for phenacyl-based onium salt photoinitiators [24-27].

Carbazole-containing compounds such as *N*-vinylcarbazole (NVC), have been demonstrated to interact with onium salt photoinitiators accelerating the rate and efficiency of cationic polymerizations. The use of carbazole-containing compounds as photosensitizer for onium salts in ring opening cationic polymerization of epoxide monomers has been investigated [28, 29]. A photosensitization mechanism based on photoinduced electron transfer reactions was proposed. Moreover, Lalevée and co-workers reported the use of NVC as an additive for free radical promoted cationic polymerization of epoxide monomers [30]. NVC was used in the presence of iodonium salts so as to convert the hardly oxidizable radicals formed upon irradiation of various photoinitiating systems under visible light to easily oxidizable ones. Upon addition of radicals to the vinyl double bond of NVC, radicals of NVC were formed which could be easily oxidized by onium salts to form initiating cationic species. In a recent study, NVC was used to act as photoinitiator, additive an monomer simultaneously [31].

1.1 Purpose of Thesis

In this thesis, a new phenacyl-type photoinitiator exhibiting light absorption characteristics at higher wavelengths was designed and synthesized. The photoinitiator was synthesized by quaternizing ethyl carbazole using phenacyl bromide and a subsequent ion exchange to afford the phenacyl ethyl carbazolium hexafluoroantimonate (PECH) photoinitiator. Bearing conjugated carbazole units, PECH exhibited excellent optical characteristics in the near UV region, which makes it advantageous over other phenacyl-based structures. Optical behavior of the photoinitiator is carefully evaluated and free radical photopolymerization of a series of vinyl monomers has been successfully achieved under UV light irradiation.

In contrast to the general behavior of phenacyl-based photoinitiators in the photoinitiation of cationic polymerization, PECH failed to initiate the cationic polymerization. It has been suggested that this may be due to the tendency of the photo-fragments to couple through carbazole units and thermodynamically unfavorable redox potential of the salt. The combination of photo-fragments could probably lead to new possibilities for the new synthesis of conducting polymers with potential applications in various areas.

2. THEROTICAL PART

2.1 Photoinitiated Polymerization

During the most recent decades, photopolymerization takes an interest in industrial and academic field due to its excellent properties. Photopolymerization has many advantages if compared with thermal and redox curing which the systems are heated to obtain active species. For example, spatial control and temporal control of photopolymerization make it attractive for rapid and inexpensive processing of polymeric composites and initiation reaction is achieved by the control of the initiating light because rate of the polymerization product is independent from temperature. Furthermore, by using photochemical processes active centers are produced more quickly and efficiently than thermal processes, they operate at room temperatures, in order to reduce material cost it is used with solvent free systems hereby volatile organic compound emission have been eliminated. Photochemical routes provide high production rates and it needs less energy for curing more than thermal polymerizations.

In recent years, photopolymerization technologies have a lot of commercial applications due to its unique properties. In practice, these applications have been sorted into some categories:

i) utilizing from solubiliy properties of this polymerization, printed wiring board resists, and printing plates [32, 33],

ii) by application of adhesion modulation in photopolymer materials, printing products such as printing inks [34] and printing plates [35]

iii) by changing of refractive index in photopolymer, liquid cyristal displays and holographic devices,

iv) by adjusting electrical conductivity on the surface of a photopolymer, film protective furnitures are produced [32].

In addition to these, photopolymerization technologies are widely used in areas such as coatings for biosensors and electrodes, coatings for optical fibers , textile fibers

and polyester films, membrane materials, ion-selective electrodes, production of contact lenses and implants, hydrogels, the immobilization of enzymes and dental applications [36-39].

Photopolymerization is typically a process that use light energy to initiate chain reaction to obtain polymeric materials. The ractive specises can be free radicals, anion or cation, which are formed from photosensitive namely photoinitiators and/or photosensitizers, by UV-Vis light irradiation (Figure 2.1) [40]. If some specific properties are needed such as flexibilty, colours and toughness, photopolymerization systems are composed of monomer(s), the initiator(s), any photosensitizers and other additives.

The reaction is started with absorbtion of light by photoinitiators and then active center is produced. With the absortion of light by the initiator, some type of decomposition is occur by hydrogen abstraction or electron transfer reaction. The most important point here is that active centers contain a radical species which include an unpaired electron [41, 42]. After generation of active centers, first the initiating group is activated and then reacted with a double bond to form a covalent bond and a new active side on the second carbon of the double bond and propagation and termination then take place in the same way as thermal polymerization systems.

Even though photo polymerization follows the same laws of chemistry as do the thermal polymerizations in kinetic treatment, important differences appear during the initiating stage. Active species such as free radicals come from thermal degradition in thermal polymerization but on the other side in photopolymerization free radicals are produced from photolyses of the photoinitiators.

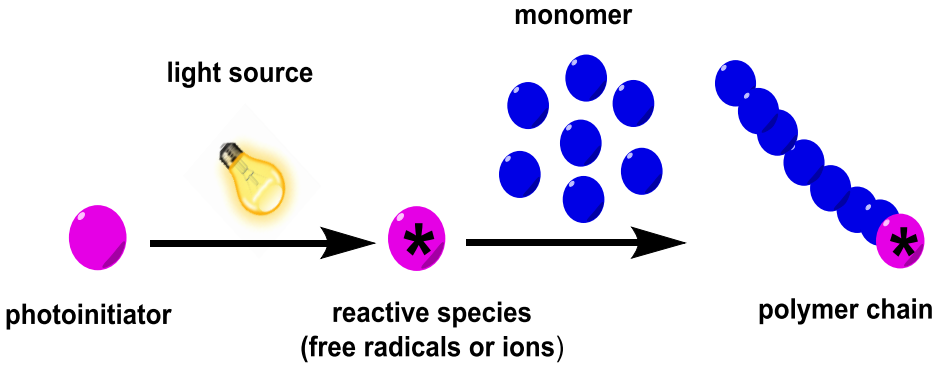


Figure 2.1 : General presentation of photoinitiated polymerization.

2.1.1 Photoinitiated free radical polymerization

Photoinitiated polymerization is one of the most efficient techniques in polymer community. The use of light as driving force to initiate the process has made it possible to reduce the fabrication process cost and to suppress some drawbacks rising in thermal processes under milder conditions [1].

It has been applied in various applications such as coatings, adhesives, inks, printing plates, optical waveguides, microelectronics, dental fillings and fabrication of 3D objects etc. The role of light in such systems is mainly confined to the very first step of the reaction that is to form active initiating species such as free radicals or cations to initiate polymerization.

Photoinitiated free radical polymerization is one of the most widely employed route in industrial applications because of its applicability to a wide range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range.

It consists of four distinct steps, shown in Figure 2.2:

i) photoinitiation step involves absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.

ii) propagation step involves repeated addition of monomer units to the chain radical produces the polymer backbone.

iii) chain transfer step involves termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and formation of new radicals capable of initiating other chain reactions.

iv) termination step involves termination of chain radicals by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

Photoinitiation:

$$PI \xrightarrow{h\nu} PI^* \qquad \text{(Absorption)}$$

$$PI^* \longrightarrow R_1^{\bullet} + R_2^{\bullet} \qquad \text{(Radical Generation)}$$

$$R_1^{\bullet} + M \longrightarrow R_1{-}M^{\bullet}$$

Propagation:

$$R_1{-}M^{\bullet} + M \longrightarrow R_1{-}MM^{\bullet}$$

$$R_1{-}MM^{\bullet} + (n\text{-}2)M \longrightarrow R_1{-}M_n^{\bullet}$$

Transfer:

$$R_1{-}M_n^{\bullet} + R{-}H \longrightarrow R_1{-}M_n{-}H + R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow R{-}M^{\bullet}$$

Termination:

$$R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1{-}M_{n+m}{-}R_1$$

$$R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1{-}M_n{-}R_2$$

$$R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1{-}M_n + R_1{-}M_m$$

$$R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1{-}M_n + R_2$$

Figure 2.2 : Elementary reactions in free radical photopolymerization.

Photoinitiators, play a major role in photopolymerization. They are generally classified into two classes of *Type I* (also known as α-cleavage) and *Type II* (hydrogen abstraction type). Disassociation of *Type I* photoinitiators upon absorption of light directly gives rise to the initiating radicals, while in *Type II* systems abstraction of a hydrogen by photoexcited (triplet state) photoinitiator encounters for the formation of radicals.

Photoinitiated radical polymerization may be initiated by both Type I which upon irradiation undergo an α-cleavage process to form two radical species and Type II initiators which are second class of photoinitiators and are based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical.

2.1.1.1 *Type I* photoinitiators (unimolecular photoinitiator system)

Initiating radicals, formed by direct photofragmentation process (α or less common β cleavage) of *Type I* photoinitiators upon absorption of light, are capable of inducing polymerization.

The photoinitiator forms an excited singlet state, which then undergoes rapid intersystem crossing to form a triplet state. In the triplet state, two radicals (benzoyl and benzyl radicals) are generated by α-cleavage fragmentation. The benzoyl radical is the major initiating species, while, in some cases, the benzyl radical may also contribute to the initiation (Figure 2.3).

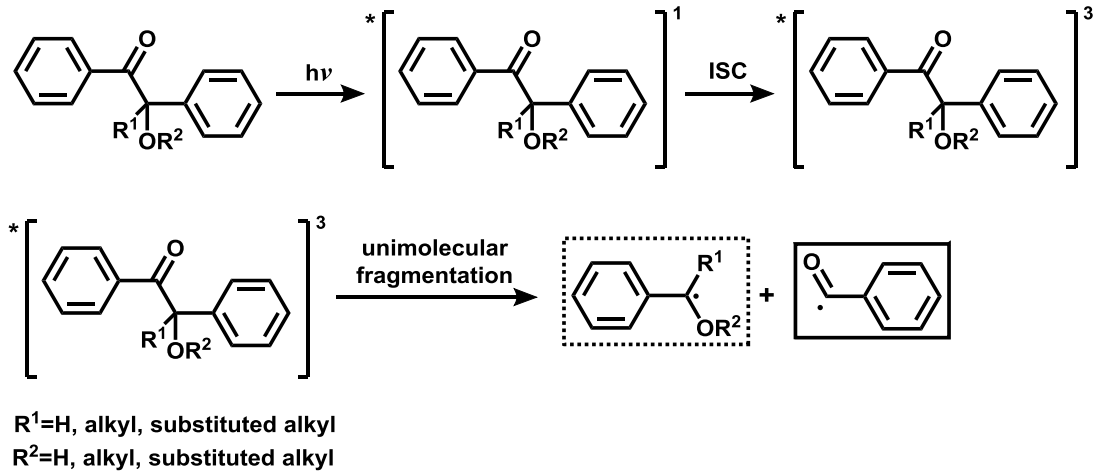
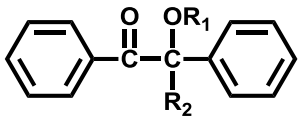
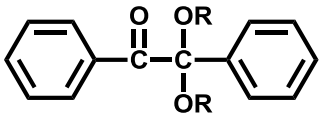
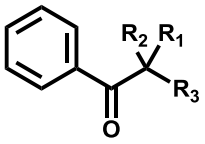
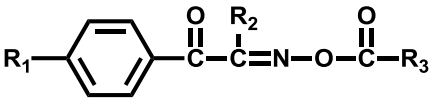
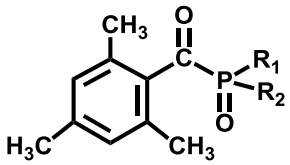
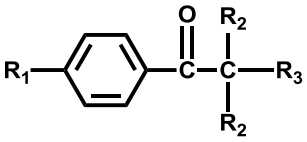


Figure 2.3 : Formation of initiating radicals from decomposition of a *Type I* photoinitiator.

Most of the *Type I* photoinitiators are aromatic carbonyl compounds with convenient substituents. Benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides are the most proficient ones (Table 2.1) [43-46].

The photoinduced α-cleavage reaction is not only or only very little influenced by triplet quenchers including styrene, owing to the short lifetime of the excited triplet state and this situation makes benzoin photoinitiators particulary useful for industrial appliations involving styrene monomer. it must be specified that in regards to the pratial appliations, benzoin deriaties are storable for restricted time at ambient temperature.

Table 2.1 : Structures of typical *Type I* radical photoinitiators.

Photoinitiators	Structure	λ_{max} (nm)
Benzoin ethers	 R_1 = H, alkyl R_2 = H, substituted alkyl	323
Benzil ketals	 R = CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3, H R_3 = C_6H_5, OH	340
Benzyl oxymes	 R_1 = H, SC_6H_5 R_2 = CH_3, C_6H_{13} R_3 = C_6H_5, OC_2H_5	335
Acylphosphine oxides	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph, C_2H_5 R_3 = $N(CH_3)_3$, morpholine	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph or C_2H_5 R_3 = $N(CH_3)_3$, morpholine	320

2.1.1.2 *Type II* photoinitiators (bimolecular photoinitiator system)

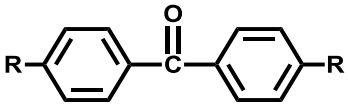
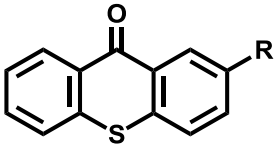
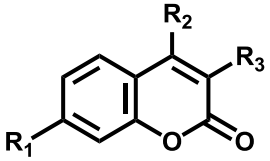
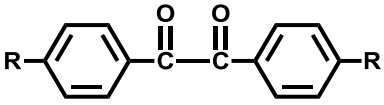
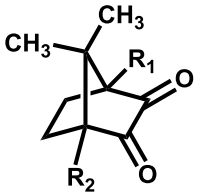
Because of certain compounds' excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy), the excited states of them do not undergo *Type I* reactions .

$$PI \xrightarrow{h\nu} PI^{*} + COI \xrightarrow{k} R_1 \cdot + R_2 \cdot \qquad \textbf{(2.1)}$$

$$\frac{d[R_1 \cdot]}{dt} = \frac{d[R_2 \cdot]}{dt} = k[PI^{*}]\,[COI] \qquad \textbf{(2.2)}$$

The excited molecule can, however, react with another component of the polymerization mixture (co-initiator (COI)) to produce initiating radicals **(2.1)**. In this case, radical generation follows second-order kinetics **(2.2)**. In these systems, photons are absorbed in the near UV and visible wavelengths. Photoinitiators of *Type II* system including benzophenones, thioxanthones, camphorquinones, benzyls, and ketocoumarins are listed in Table 2.2.

Table 2.2 : Structures of typical *Type II* photoinitiators.

Photoinitiators	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 $R_1 = N(C_2H_5)_2, N(CH_3)_2$ $R_2 = CH_3$, cyclopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340
Camphorquinones	 $R_1 = CH_3$, H R_2 = H, CH_3	470

In *Type II* systems, radicals are generated by two distinct pathways:

(i)hydrogen abstraction

(ii)photo-induced electron transfer process.

(i) Hydrogen abstraction

Photoinitiators that proceed via a hydrogen abstraction mechanism are demonstrated by combination of benzophenone and a hydrogen donor (Figure 2.4). When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.

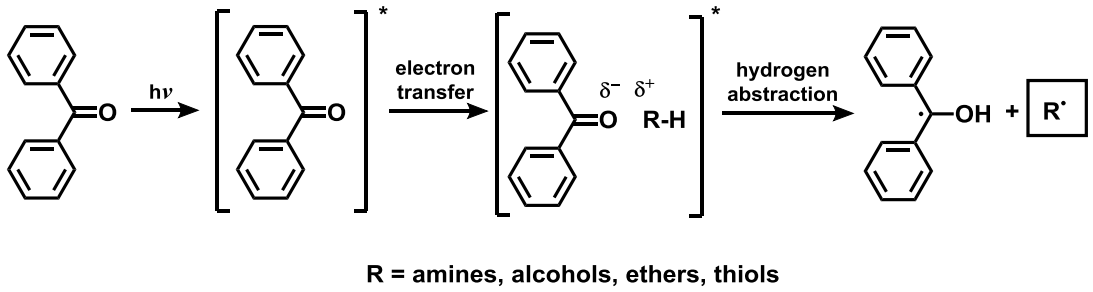


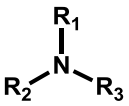
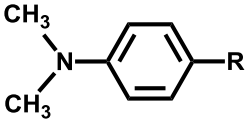
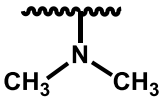
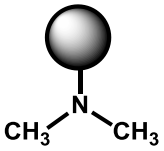
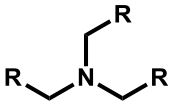
Figure 2.4 : Formation of initiating radicals from photolysis of *Type II* photoinitiator in the presence of suitable hydrogen donor.

The co-initiators such as an amine, ether, thiol or alcohol with an abstractable α-hydrogen are also categorized in Table 2.3.

Lately, thiol and carboxylic acid derivatives of thioxanthones have been stated to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [37-39].

Alternative approach concerns the attachment of both chromophoric and hydrogen donating groups into polymer chains. This way, the odor and toxicity problems observed with the conventional photoinitiators and amine hydrogen donors were overcome.

Table 2.3 : Structures of typical *Type II* hydrogen donors.

Hydrogen Donors	Structure
Aliphatic Amines	 $R_1 = C_2H_5, CH_3, CH(CH_3)_2$ $R_2 = C_2H_5, C_2H_4OH, CH(CH_3)_2$ $R_3 = C_2H_5, C_2H_4OH, CH(CH_3)_2$
Aromatic Amines	 R = H, COOH, $COOCH_2CH_3$, $COOC_8H_{17}$
Polymeric Amines	 polymer = poly(methyl methacrylate)s, polyacrylates or polyurethanes
Dendrimeric Amines	 core = polyglycerols or poly(propylene imine)s
Acrylated Amines	 R = acrylates or methacrylates
Alcohols	R—OH R = isopropyl, hydroxyethyl methacrylate
Ethers	R—O—R R = tetrahydrofuran, benzodioxole poly(ethylene oxide), poly(propylene oxide), poly(tetrahydrofuran)
Thiols	R—SH R = benzimidazole, benoxazole, benzthiazole, thioxanthone

(ii) Photoinduced electron transfer reactions and subsequent fragmentation.

Photoinduced electron transfer is a more general process which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds can act as either an electron donor with the coinitiator as an electron

acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (Figure 2.5).

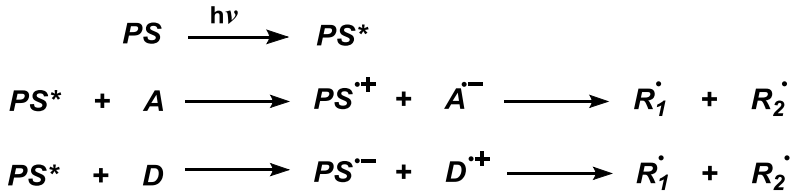


Figure 2.5 : Free radical generation by photosensitization.

The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation **(2.3)** [119] is negative.

$$\Delta G = F\,[E_{½}^{ox}\,(D/D^{+\bullet}) - E_{½}^{red}\,(A/A^{-\bullet})] - E_{PS} + \Delta E_c \qquad \textbf{(2.3)}$$

where, F = Faraday constant,

$E_{½}^{ox}$ $(D/D^{+\bullet})$ = oxidation potential of donor,

$E_{½}^{red}$ $(A/A^{-\bullet})$ = reduction potential of acceptor,

E_{PS} = Singlet state energy of the photosensitizer,

ΔE_c = Coulombic stabilization energy.

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems. Dyes comprise a large fraction of visible light photoinitiators because their excited electronic states are more easily attained. Co-initiators, such as tertiary amines, iodonium salts, triazines, or hexaarylbisimidazoles, are required since dye photochemistry entails either a photo-reduction or photo-oxidation mechanism. Numerous dye families are available for selection of an appropriate visible initiation wavelength; examples of a thiazine dye (with an absorption peak around 675 nm), acridine dyes (with absorption peaks around 475nm), xanthene dyes (500–550 nm), fluorone dyes (450–550 nm), coumarin dyes (350–450 nm), cyanine dyes (400–750 nm), and carbazole dyes (400 nm) [47-50]. The oxidation or reduction of the dye is dependent on the co-initiator; for example, methylene blue can be photo-reduced by accepting an electron from an amine or photo-oxidized by transferring an electron to benzyltrimethyl stannane [47]. Either mechanism will

result in the formation of a free-radical active center capable of initiating a growing polymer chain.

2.1.2 Photoinitiated cationic polymerization

Much effort has been devoted to free radical photopolymerizations mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers [4]. Although the most popular industrial applications are based on the photo-initiated free radical polymerization there are some drawbacks associated with this type of polymerization. For instance, free radical species are inhibited by molecular oxygen and inhbites almost polymerization based on free radicals. Moreover, post-cure limitations, which may affect the properties of the final product and toxicity of the monomers are another drawbacks. Several advantages of the photo-initiated cationic polymerization over the photoinitiated free radical polymerization have also been reported [51]. Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity [40]. Furthermore, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation. General scheme for photoinduced cationic polymerization is depicted in Figure 2.6. A photo-sensitive compound, namely photoinitiator (PI), absorbs incident light and undergoes decomposition leading to production of initiating species. Active species, namely a radical cation ($R^{+\bullet}$) in turn, react with cationic polymerizable monomers (M), and yield polymer.

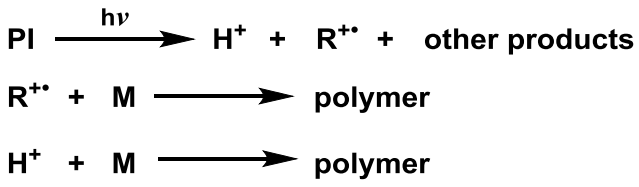


Figure 2.6 : General scheme of photoinitiated cationic polymerization.

Photoinduced cationic polymerization can be initiated by a number of agents including Lewis and Brønsted acids, carbonium ions and onium salts. A key feature of cationic polymerization is the use of acids possessing anions of very low nucleophilicity, which do not terminate the polymerization process. Therefore, most cationic photoinitiators are based on salts of non-nucleophilic anions such as BF_4^-,

PF_6^-, AsF_6^- and SbF_6^-. Generally, molecular weights and percentage conversion increase in the order of $BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$.

Cationic photoinitiators are generally divided into two classes, ionic and non-ionic photoinitiators. These classes consist of structurally related compounds which undergo similar photochemical reactions.

1) Ionic cationic photoinitiators: Onium salts and organometallic salts

2) Non-ionic cationic photoinitiators: Organosilanes, latent sulphonic acids and miscellaneous non-ionic compounds

Onium salts are the most commonly used cationic photoinitiators. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [52]. Each of these componenets has specific function and can be varied independently depending on the purposed application. The cation of an onium salt is the light absorbing portion of the compound and its structure determines the wavelength sensitivity and quantum yield of the initiator. In addition, the character of the cation also has an influence on the excited state chemistry and whether or not the onium salt can undergo photosensitization with a photosensitizer. In recent years, onium salts with highly nucleophilic counterions such as Cl^-, Br^- and I^- have also been used in conjuction with Lewis acids [53-56]. Different types of onium salts are shown in Figure 2.7.

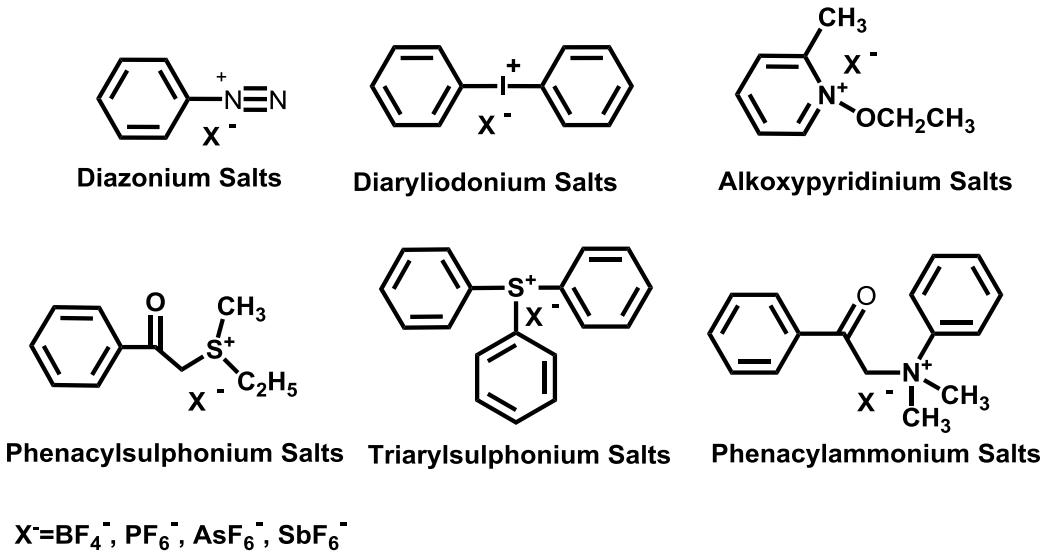


Figure 2.7 : Types of onium salt photoinitiators.

So far, the most frequently used onium salts are diaryliodonium [57, 58], triarylsulfonium [59, 60], alkoxypyridinium [61, 62] and phenacyl [13, 16, 19, 63-68] salts with non-nucleophillic counter ion that mainly absorb the light in the region between 225 and 350 nm for photoinitiated cationic polymerization.

Most photoinitiators, used in cationic photopolymerization mainly absorbs light between 225 to 350 nm. For practical applications, however, they are expected to absorb light at quite longer wavelengths. Provided the systems thus obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms:

1. Classical energy transfer: The electronic excitation energy is transferred from the excited additive (sensitizer) to the onium salt initiator producing the excited state of the latter. The route of onium salt decomposition often differs from that observed for direct photolysis of the onium salt [26, 69-72].

2. Free radical promoted: Many photolytically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerizations [73-75].

Polymerizations initiated via addition-fragmentation reactions can also be classified as an initiation process involving radicalic species. The principle of this class of reactions consists in the reaction of a photolytically formed radical with an allyl–onium salt generating a radical cation intermediate. These reactive species undergo a fragmentation giving rise to the formation of initiating cations.

3. Electron transfer via exciplexes: Sensitizers such as anthracene, perylene or phenothiazone form exciplexes with onium salts. Being formed in the consequence of light absorption by the sensitizer, these energy rich complexes consist of non-excited onium salt and electronically excited sensitizer molecules. In the complexation state, electron transfer to the onium salt is observed, giving rise to positively charged sensitizer species [76, 77].

Notably, above decsribed initiation methods do not involve the electronic excitation of the onium salt. Consequently, the initiation mechanisms are entirely different from that found for direct photolysis of onium salts [78-81].

2.1.3 Photoinitiated anionic polymerization

Anionic photopolymerization had received less attention compared to cationic and free radical counterparts [82]. However, anionic photopolmerization recieve further attention after introduction of a new initiating system depending on *trans*-$Cr(NH_3)_2(NCS)_4^-$(Reineckate anion). In fact, irradiation of ligand field absorption bands of transition metal complexes results in ligand substitution reactions. This process can be employed for the controlled photogeneration of anions from a stable precursor. *trans*-$Cr(NH_3)_2(NCS)_4^-$ is considered as an ideal anion source since K^+[*trans*-$Cr(NH_3)_2(NCS)_4^-$] is readily soluble in a variety of organic solvents, resistant to thermal substitution in nonhydroxylic media, and its quantum efficiency is quite high (> 10%) for releasing of NCS^- (Figure 2.8) upon ligand field excitation with near-UV/Vis light [83-85]. In the presence of a monomer containing electron-withdrawing substituents to stabilize the negative charge, such as ethyl α-cyanoacrylate, anionic polymerization is initiated.

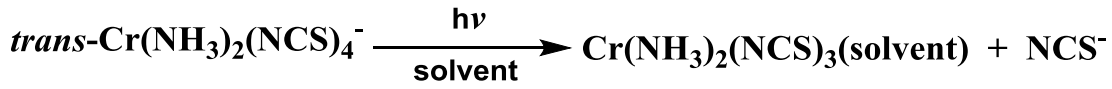


Figure 2.8 : Generation of anionic initiating species from *trans*-$Cr(NH_3)_2(NCS)_4^-$.

In another report, acyl-substituted ferrocenes, namely benzoylferrocene and 1,1'-dibenzoylferrocene, were utilized as photoinitiator for the anionic polymerization of ethyl α-cyanoacrylate [86].

Generation of anionic initiating species is schematized in Figure 2.9. $Pt(acac)_2$ or a cyclopentadienyl complex of Fe or Ru have been also utilized as anionic photoinitiators [87].

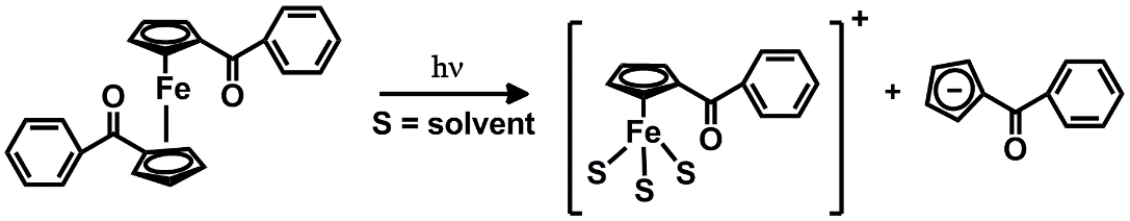


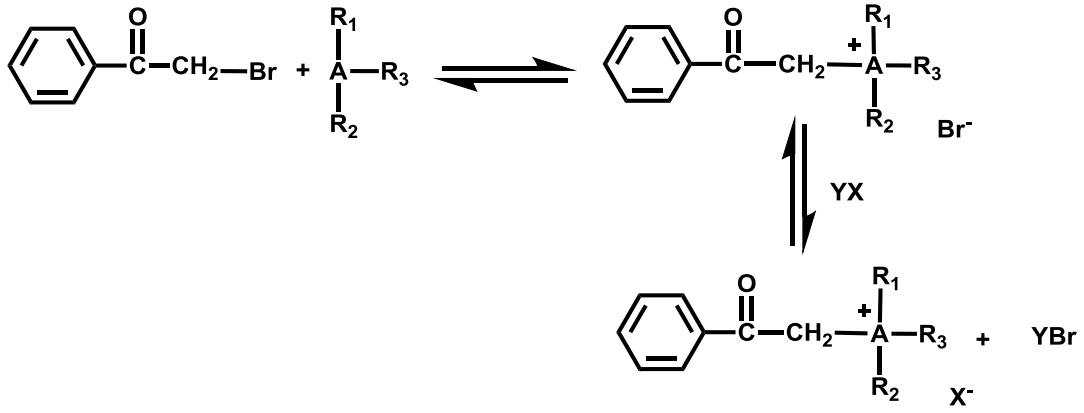
Figure 2.9 : Generation of anionic species from photolysis of 1,1'-dibenzoylferrocene.

2.1.4 Phenacyl type photoinitators

Onium salts, namely sulfonium, phosphonium, ammonium, and pyridinium salts containing phenacyl group are photoinitiators appropriate for the polymerization of monomers such as oxiranes and vinyl ethers, which are not polymerizable by a free-radical mechanism [66].

The initiation is accomplished by direct or indirect (sensitized) photolysis of the salts.

Commonly, phenacyl-based onium salts are synthesized by the reaction of phenacyl halides with the corresponding heteroatom nucleophiles followed by anion exchange with potassium or sodium salts with non-nucleophlic counteranions such as, SbF_6^-, PF_6^-, AsF_6^-, etc. Bromides were used as the halides to afford the salts with the improved yields (Figure 2.10).



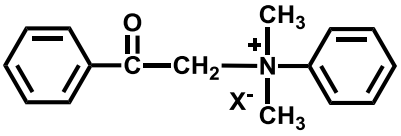
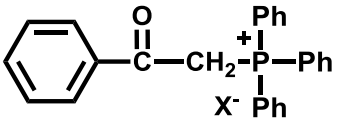
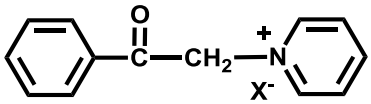
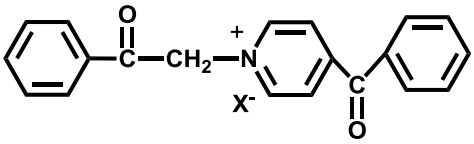
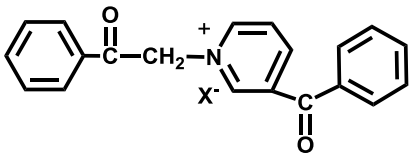
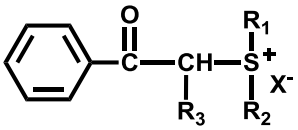
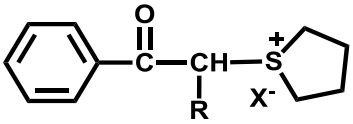
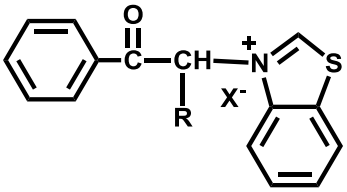
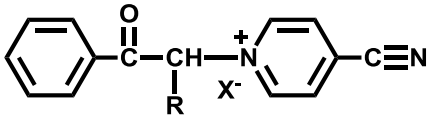
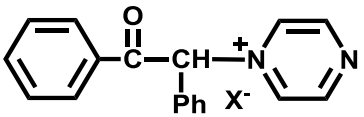
A	R_1	R_2	R_3
N	CH_3	CH_3	Ph
P	Ph	Ph	Ph
S	CH_3	$C_{12}H_{25}$	-
Y: Na, K; **X**: SbF6, PF6, AsF6, etc.			

Figure 2.10 : Synthesis of phenacyl onium salts.

The light-absorbing chromophore in phenacyl-type onium salts is the phenyl ketone group. Therefore, most of the primary reactions occur through the excitation of this group.

However, depending on the heteroatom in the salt structure, the photodecomposition may vary. The structures and absorption characteristics of the various families of pheancyl based onium salts are shown in Table 2.4.

Table 2.4 : The structures and absorption characteristics of the various families of pheancyl based onium salts.

Salt Structure	Abbreviation	λ_{max} (nm)	References
	PDA^+X^-	249, 279	[14, 18]
	PTP^+X^-	249, 279	[18]
	PPy^+X^-	249, 279, 438	[13, 16-18]
	PBP^+X^-	252, 507	[16]
	$PPBP^+X^-$	252, 442	[16]
	$PDAS^+X^-$	250, 280	[13, 63, 64, 68, 72, 88]
	$PTMS^+X^-$	250, 290, 315	[13, 68]
	PBT^+X^-	255, 264	[17]
	PCP^+X^-	253, 277, 483	[17]
	PPz^+X^-	256, 395, 461	[17]

$X^- = SbF_6^-, PF_6^-, BF_4^-, AsF_6^-, -SC(S)N(Et)_2$, etc.

2.1.4.1 Phenacylsulfonium salts

A novel simplified method for the synthesis of phenacylsulfonium salts was reported by Crivello and Kong [63]. The method involves a one-pot reaction of phenacyl bromides or their aryl counter parts with the appropriate dialkyl sulfides in the presence of an alkali metal salt with desired anion (Figure 2.11).

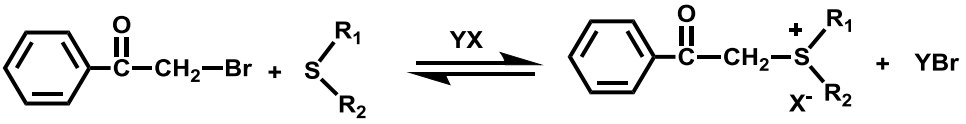


Figure 2.11 : Synthesis of phenacylsulfonium salt.

In the case of phenacylsulfonium, the photolysis in the absence of monomers is essentially reversible and, the ylides rapidly react with the protonic acid to afford the starting salt (Figure 2.12). The detailed mechanistic studies revealed that intramolecular hydrogen abstraction of photoexcited salt from the carbon atoms neighboring sulfur atom is followed by internal electron transfer, the polymerization is illustrated in Figure 2.13.

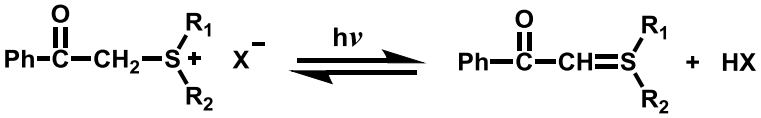


Figure 2.12 : The pholtolysis of phenacylsulphonium salt.

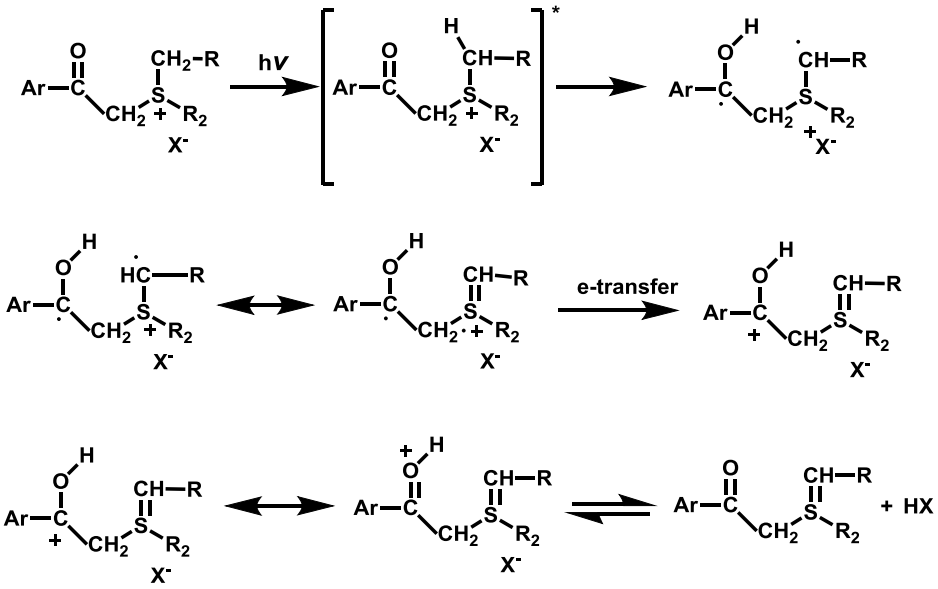


Figure 2.13 : Photoinitiated cationic polymerization mechanism by using phenacyl sulphonium salts.

2.1.4.2 Phenacylammonium salts

This simple one-pot reaction was also used for the synthesis of the other phenacyl onium salts. Accordingly, phenacyl bromide was reacted with *N*,*N*-dimethyl aniline, triphenylphosphine, and pyridine to yield the respective salts [67].

In this approach, the precipitation of insoluble NaBr or KBr depending on the initial salt strongly shifts the two simultaneous equilibrium reactions toward the desired final product.

Interestingly, phenacyl-type onium salts other than sulfonium salts undergo irreversible photolysis leading to fragmentation of the photoinitiator (Figure 2.14) [19, 89]. Electronically excited salt may undergo heterolytic cleavage (b) resulting in the formation of phenacylium cations. It is also feasible that homolytic cleavage (a) followed by the intermolecular electron transfer (a′) essentially yields the same species.

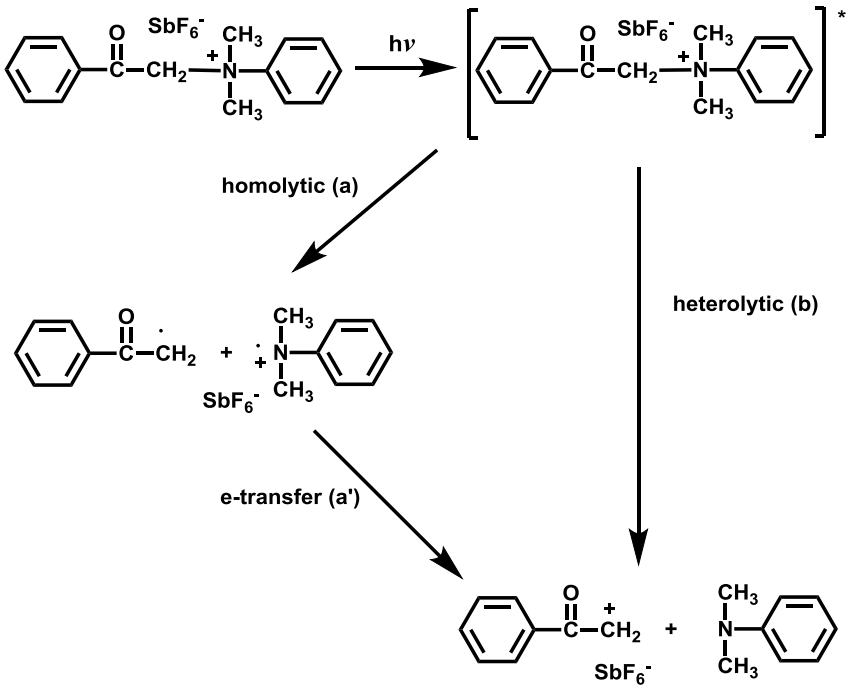
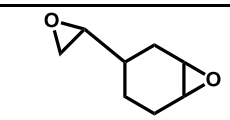
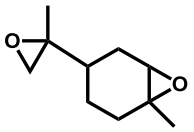
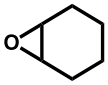
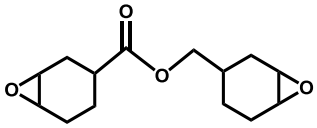
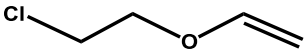
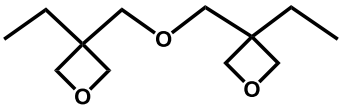
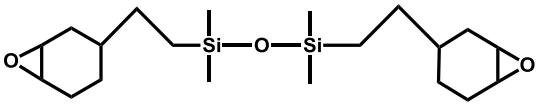
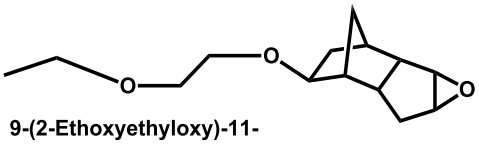
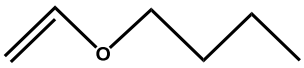
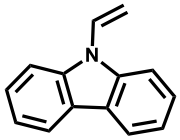
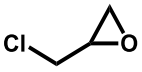
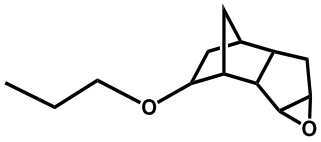
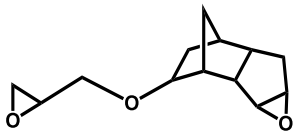


Figure 2.14 : Photolysis of phenacyl anilinium salt.

The polymerization of a wide range of cyclic ethers and vinyl monomers in systems containing the salts listed in Table 2.5 is photoinitiated upon irradiation at wavelengths at which the onium salt absorb the light directly.

Table 2.5 : Monomers used in photoinitiated cationic polymerization.

Monomer	Photoinitiator	References
 4-vinylcyclohexene dioxide	$PDAS^+X^-$	[72]
 limonene dioxide	$PDAS^+X^-$	[13, 72]
 cyclohexene oxide	PDA^+X^- PBP^+X^- $PPBP^+X^-$ PPy^+X^- $PDAS^+X^-$	[16, 19, 25, 72]
 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate	PBT^+X^- PCP^+X^- PPz^+X^- PBQ^+X^- $PDAS^+X^-$	[17, 64, 72]
 2-chloroethyl vinyl ether	$PDAS^+X^-$	[72]
 bis(3-ethyl-3-oxetanylmethyl)ether	$PDAS^+X^-$	[72]
 1,3-Di(3,4-epoxycyclohexylethyl)-1,1,1,3,3-tetramethyldisiloxane	$PDAS^+X^-$	[64]
 9-(2-Ethoxyethyloxy)-11-oxatetracyclo[6.2.1.0^{2,7}0^{4,6}]undecane	$PDAS^+X^-$	[64]
 Butyl vinyl ether	PDA^+X^-	[19]
 *N*-vinyl carbazol	PDA^+X^-	[19]
 Epichlorohydrin	$PDAS^+X^-$ $PTMS^+X^-$	[68]

 Epoxidized dicyclopentenyl propyl ether	$PDAS^+X^-$ **I**, **II**, **III**, **IV**, **V**	[88]
 Epoxidized dicyclopentenyl glycidyl ether	$PDAS^+X^-$ **I**, **II**, **III**, **IV**, **V**	[88]

Photoinitiated free-radical and zwitterionic polymerizations by using phenacyl-type salts are also possible [67]. Although phenacyl onium salts that contain counter anions with low nucleophilicity, are efficient and convenient compounds to generate Lewis bases photochemically, they suffer from the drawback of the termination of the anionic species by the photofragments formed from these compounds. The phenacylium cations stabilized with non-nucleophilic counteranions can react with the initiating and propagating centers. For this reason, for potential application of these salts as photoinitiators for anionic polymerization it is necessary to equip them with counteranions with higher nucleophilicity.

Electronically excited salt may undergo heterolytic cleavage resulting in the formation of phenacylium cations. Alternative pathway in which homolytic cleavage followed by electron transfer essentially yields the same species capable of initiating polymerizations oxiranes and vinyl ethers.

Notably, phenacylium cation is converted to covalently bonded inert compound as a result of the combination of the cation with dithiocarbamate anion and free Lewis base, dimethylaniline is liberated in Figure 2.15.

If the polymerization mechanism involved only free radical species, the polymerization would be completely inhibited by a radical scavenger. Accordingly, if the polymerization was initiated via a zwitterionic mechanism, sample containing protonation agent would yield no polymer.

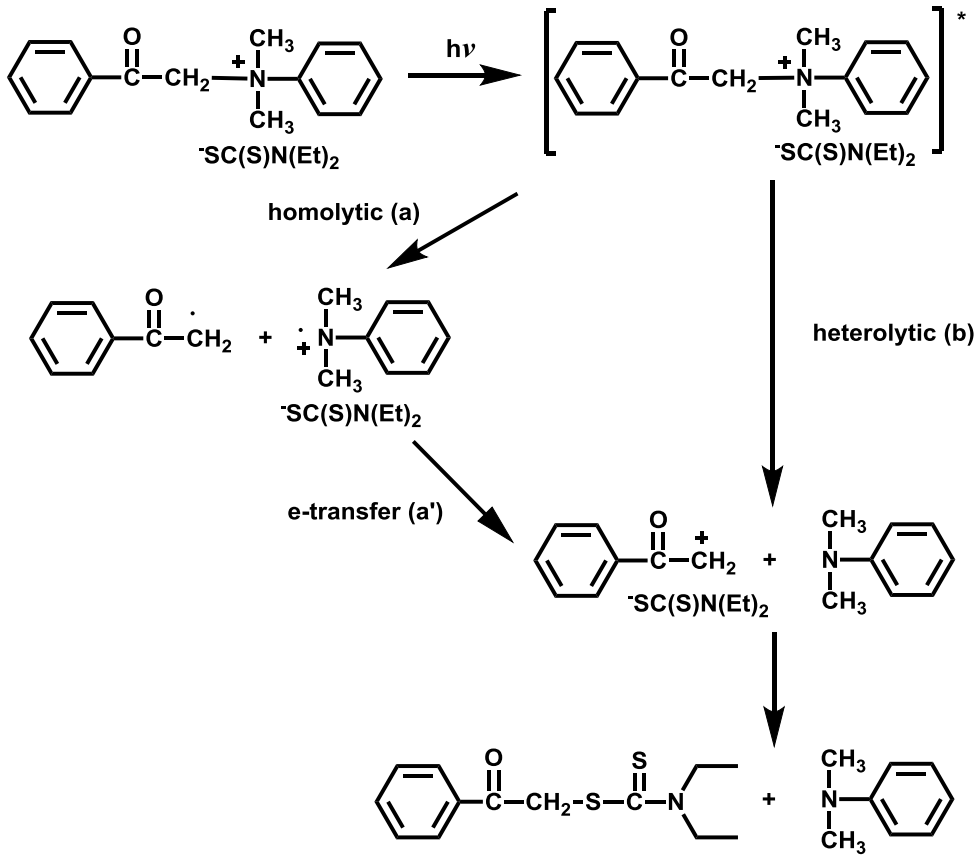


Figure 2.15 : Formation of phenacyl dithiocarbamate by coupling of phenacylium cation and dithiocarbamate anion.

It is therefore most probable that both radical and zwitterionic mechanisms are responsible for the initiation. Phenacyl radicals induce freeradical polymerization while dimethylaniline initiates zwitterionic polymerization according to the following reactions in Figure 2.16.

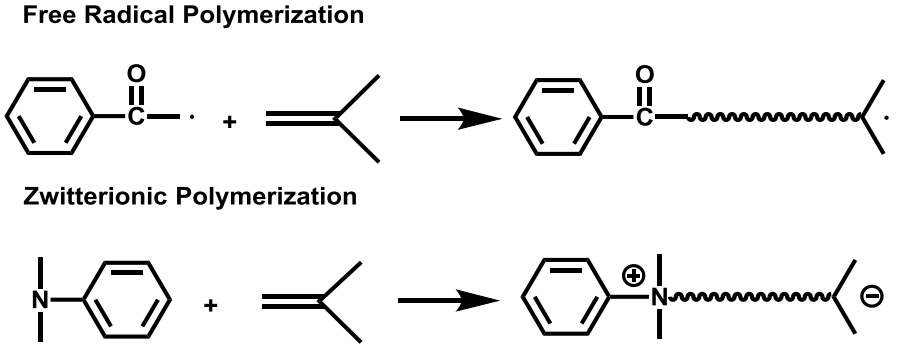


Figure 2.16 : Photoinitiated free-radical and zwitterionic polymerizations by using phenacyl-type salts.

2.1.4.3 Step-growth polymerization

In a step-growth polymerization, the molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of polymer. The different initiation, propagation, and termination steps of chain-growth polymerization are meaningless in step-growth polymerization.

Photoinduced step-growth polymerization of thiophene by onium salts is demonstrated in Figure 2.17. It was shown that besides electropolymerization, conducting polythiophenes can also be obtained by means of UV irradiation of thiophene in the presence a diphenyliodonium salt.

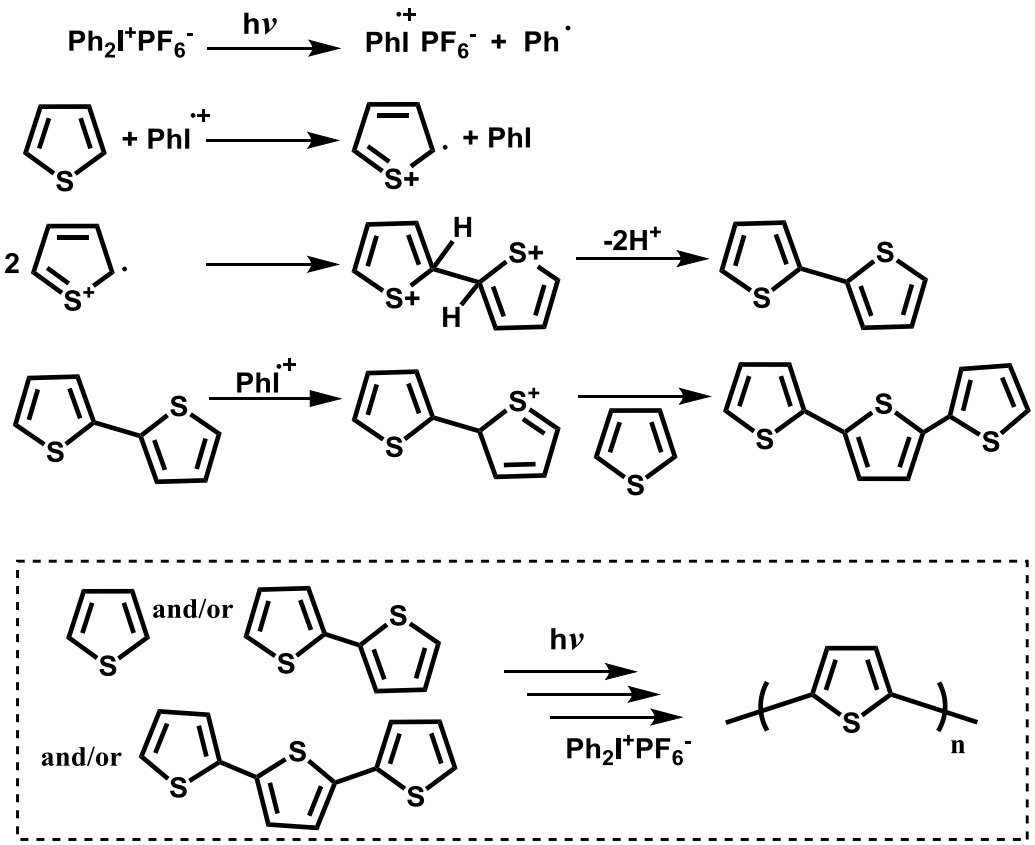


Figure 2.17 : Photoinduced step-growth polymerization of thiophene by iodonium salts.

A difunctional monomer or equal molar amounts of two different difunctional monomers are necessary at least to form a linear high molecular weight polymer. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Therefore, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer.

This route continues, each reaction of the functional groups proceeding fundamentally at the same reaction rate until over a relatively long period of time, a high molecular weight polymer is acquired [90, 91].

3. EXPERIMENTAL PART

3.1 Materials

9-Ethylcarbazole (EC; 99%, Alfa Aesar) was used without further purification.

2-Bromoacetophenone (phenacyl bromide, Merck) was used as received.

Potassium hexafluoroantimonate(V) ($KSbF_6$; 99%, Sigma-Aldrich) was used as received.

Methyl methacrylate (MMA; ≥99%, Sigma-Aldrich) was purified by passing through a basic alumina column to remove inhibitor.

Methyl acrylate (MA; 99%, Sigma-Aldrich) was purified by passing through a basic alumina column to remove inhibitor.

Styrene (St; 99%, Sigma-Aldrich) were purified by passing through a basic alumina column to remove the inhibitor prior to use.

N-Vinylcarbazole (NVC; 98%, Sigma-Aldrich) was crystallized from ethanol.

Ethylene glycol dimethacrylate (EGDMA, 98%; Sigma-Aldrich) was used without any purification.

2,2-Dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals) was used as received.

All other solvents were purchased from Merck and purified by conventional procedures.

3.2 Instrumentation

Light Source

A Rayonet photoreactor equipped with 16 lamps emitting at λ_{max} = 350 nm.

UV-vis spectrometer

UV-visible spectra were recorded with a Shimadzu UV-1601 spectrometer.

^{1}H-Nuclear magnetic resonance spectroscopy

^{1}H-NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with $Si(CH_3)_4$ as an internal standard at 500 MHz on a Agilent VNMRS 500 spectrometer at room temperature.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra were recorded on Perkin−Elmer FTIR Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and cadmium telluride (MCT) detector.

Gel permeation chromatography

Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456 − 42800, 1050 − 107000, and 10200 − 2890000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow-molecular-weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software.

Photodifferential scanning calorimetry

Photo-differential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a Polilight PL400 Forensic Plus light source between 320 and 500 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 40 mW cm^{-2} by a UV radiometer covering broad UV range. The measurements were carried out in an isothermal mode at 25 °C with a nitrogen flow of 20 mL min^{-1}.

Cyclic voltammetry

Cyclic voltammetry and electrochemical studies were investigated using a Voltalab 50 Potentiostat and in a three electrode cell consisting of platinum wires as the working and counter electrodes, and a silver wire as the reference electrode.

3.3 Synthesis of Phenacyl Ethyl Carbazolium Hexafluoroantimonate (PECH)

The photoinitiator PECH was synthesized according to the following procedure. Into a 100 mL round bottom flask equipped with a magnetic stirrer were placed EC (1.0 g, 5.12 mmol) and phenacyl bromide (1.02 g, 5.12 mmol) dissolved in 20 mL of 2-butanone. The solution was left stirring at room temperature for 2 hr. Afterwards, $KSbF_6$ (1.4 g, 5.12 mmol) was dissolved in 20 mL of 2-butanone and added dropwise to the mixture. The reaction mixture was allowed to stir overnight at room temperature and then the solution was filtered to remove potassium bromide which was formed during the reaction. Afterwards, the solution was poured into 50 mL of distilled water after which PECH was crystalized in aqueous media (conversion: 41%).

3.4 Photopolymerization

For a typical free radical polymerization, into a Pyrex tube were placed MMA (1 mL, 9.4 mmol), and PECH (10 mg, 1.8 $\times 10^{-2}$ mmol), and the reaction mixture was degassed with pure nitrogen gas for 20 min and tightly closed. The content was irradiated in a Rayonet photoreactor equipped with 16 lamps emitting at λ_{max} = 350 nm. After irradiation, the solution was precipitated in ten-fold excess methanol and the precipitated polymer was filtered and dried in vacuum.

3.5 Kinetics Studies by Photo-DSC

Into 1 mL of EGDMA (5.3 mmol) was added PECH (10 mg, 1.8 $\times 10^{-2}$ mmol). Approximately 10 mg of this solution was transferred to a photo-DSC pan. The sample was kept under nitrogen flow for at least 5 min to exclude oxygen from the solution. Before irradiation, it was stabilized by keeping the sample in the dark for 1 min, after which irradiation was started in an isothermal mode at 25 °C. The obtained

heat is relative to the number of reacted double bonds and the rate of polymerization (R_P) can be calculated according to Equation 3.1:

$$R_P = Q_t / (n \times E_{db}) \quad \textbf{(3.1)}$$

where Qt (J mol^{-1} s^{-1}) is the rate of heat released at time t, n the number of (meth)acrylate double bond, and Edb (J mol^{-1}) is the energy of double bond (~54400 J mol^{-1}) [92]. By integrating Equation 1, double bond conversion was calculated. Calculations were made after baseline corrections.

4. RESULTS AND DISCUSSION

4.1 Synthesis of PECH Photoinitiator

In this current work, a new phenacyl-type photoinitiator based on ethyl carbazole is reported for free radical photopolymerization of various vinyl monomers. Phenacyl ethyl carbazolium hexafluoroantimonate (PECH) photoinitiator was synthesized in a sequential, one-pot manner by quaternization of ethyl carbazole using phenacyl bromide and then ion exchange process upon addition of potassium hexafluoroantimonate (Figure 4.1).

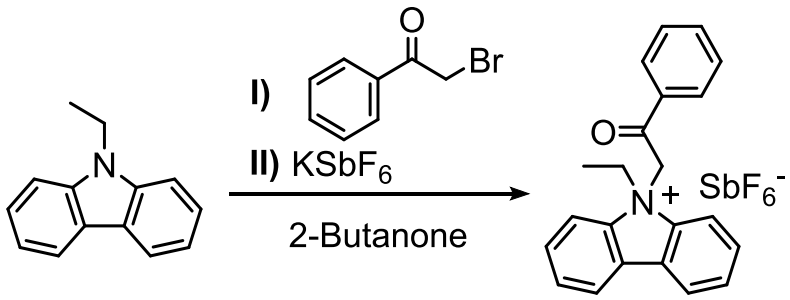


Figure 4.1 : Synthesis of phenacyl ethyl carbazolium hexafluoroantimonate photoinitiator.

The resulting photoinitiator was characterized by using 1H NMR (Figure 4.2) and FTIR (Figure 4.3) spectral analysis. Characterizing the resulting photoinitiator using FTIR spectroscopy, a new peak observed around 1700 cm^{-1} is attributed to the carbonyl stretching band of the photoinitiator.

In the design of the photoinitiator, ethyl carbazole due to its high conjugation characteristics was deliberately chosen so as to shift the spectral sensitivity of the phenacyl salt photoinitiator to higher wavelengths. As shown in Figure 4.4, the obtained photoinitiator strongly absorbs light at around 350 nm which is remarkably high as compared to previously reported phenacyl-based photoinitiators which absorb around or below 300 nm.

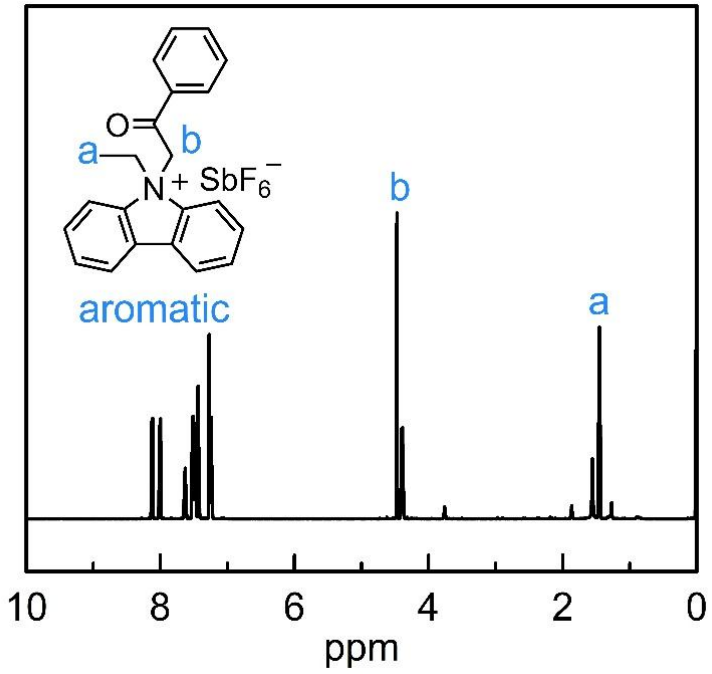


Figure 4.2 : ^{1}H NMR spectrum of phenacyl ethyl carbazolium hexafluoroantimonate.

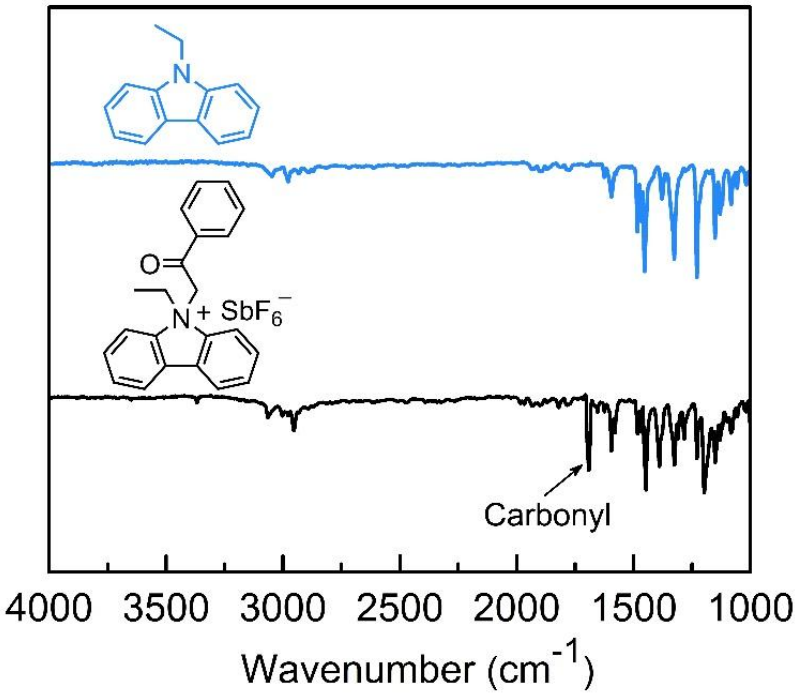


Figure 4.3 : FTIR spectra of phenacyl ethyl carbazolium hexafluoroantimonate (bottom) and ethyl carbazole (top).

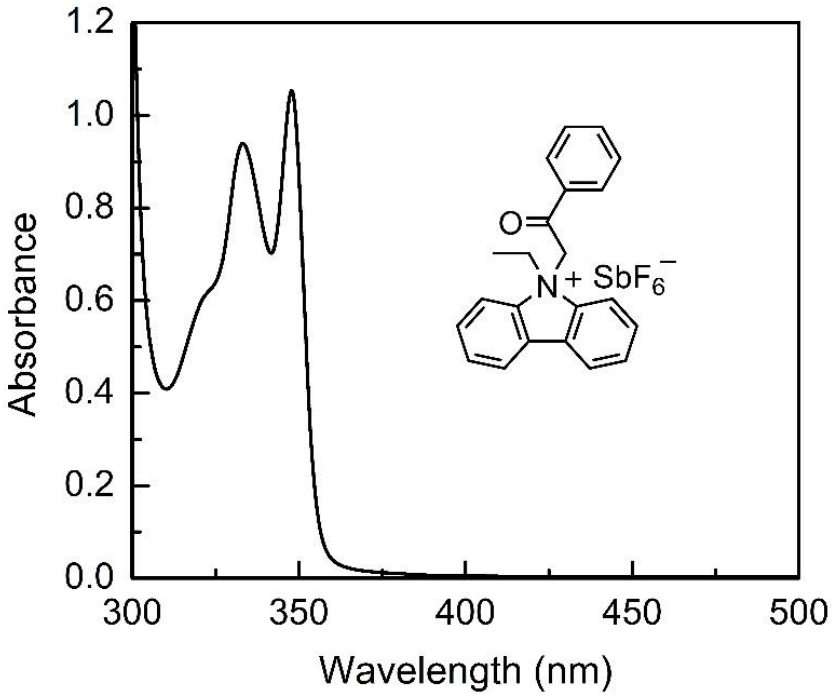


Figure 4.4 : UV-vis spectrum of PECH (0.25×10^{-3} M) in dichloromethane.

4.2 Photobleaching Expreriments

Photobleaching experiments were conducted to investigate the optical behavior of the photoinitiator under irradiation. Upon absorbing the energy of light, phenacyl-based photoinitiators have been proven to generally undergo homolytic or heterolytic bond cleavage. This results in the formation of radical or cationic species suitable for the initiation of appropriate monomers, respectively. As stated earlier, there is also a possibility of an electron transfer process converting the radicals to cationic species in the consequence of homolytic bond cleavage. As a result, these photoinitiators experience decreasing optical absorption spectra due to the loss of photoinitiator structure.

However, a different situation is encountered for the photoinitiator PECH. As illustrated in Figure 4.5, where the real-time UV-vis spectral changes are recorded, upon irradiation at 350 nm, the absorption of the solution increases and broadens. This phenomenon was attributed to the extension of conjugation during the irradiation. As previously suggested by Crivello et al., [93] the radical cations formed during the homolytic bond cleavage tend to interact with each other coupling through carbazole unities.

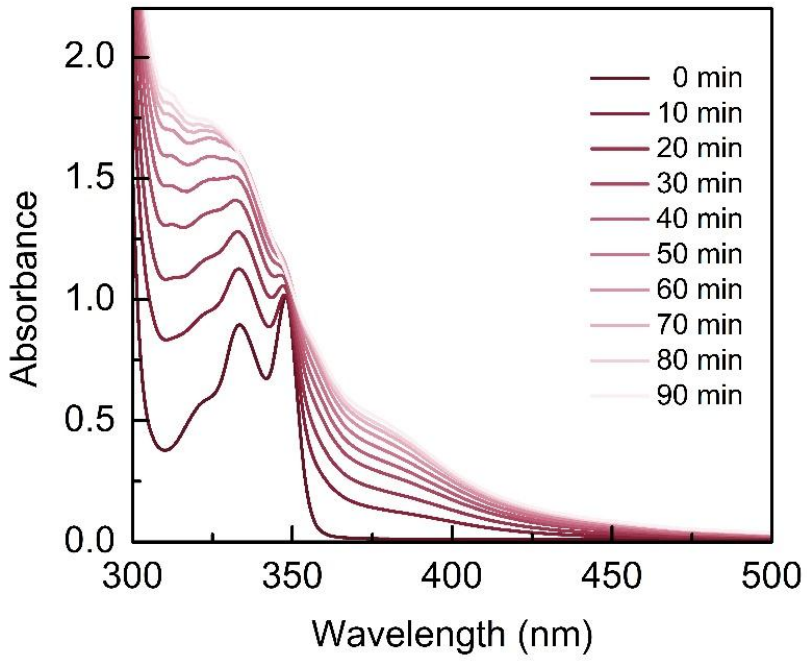


Figure 4.5 : UV-vis optical changes of PECH photoinitiator under 350 nm light irradiation; [PECH] = 0.25×10^{-3} M.

4.3 Photoinitiated Free Radical Polymerization

To investigate the applicability of this photoinitiator in the initiation of polymerization, a series of vinyl monomers including methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), and *N*-vinylcarbazole (NVC) were used. Table 4.1 summarizes the results of these experiments.

Table 4.1 : Photoinduced polymerization using phenacyl ethyl carbazolium hexafluoroantimonate for a variety of vinyl monomers [a].

Entry	Monomer	Time (min)	Conversion (%) [b]	M_n (g mol^{-1}) [c]	M_w/M_n [c]
1	MMA	60	64	26,600	3.3
2 [d]	MMA	60	9	9,100	4.1
3	MA	35	54	40,600	2.6
4	St	90	21	30,900	1.9
5 [e]	NVC	60	36	1,300	11.1

[a] Experimental conditions: λ_{max} = 350 nm, PECH = 1.8×10^{-2} mmol, and monomer = 9.4 mmol.
[b] Conversions determined gravimetrically.
[c] Number-average molecular weight (Mn) and molecular weight distribution (M_w/M_n) were measured by gel-permeation chromatography (GPC).
[d] Control experiment performed in the presence of ethyl carbazole.
[e] Performed in dichloromethane as solvent.

Polymerization of all monomers was successfully achieved with relatively high monomer conversions using PECH under UV light irradiation. As a control experiment, polymerization of MMA was attempted in the presence of the precursor ethyl carbazole which resulted in a much lower monomer conversion.

The initiation mechanism of free radical polymerization is depicted in Figure 4.6 which involves the formation of free radicals capable of initiating free radical polymerization by homolytic bond.

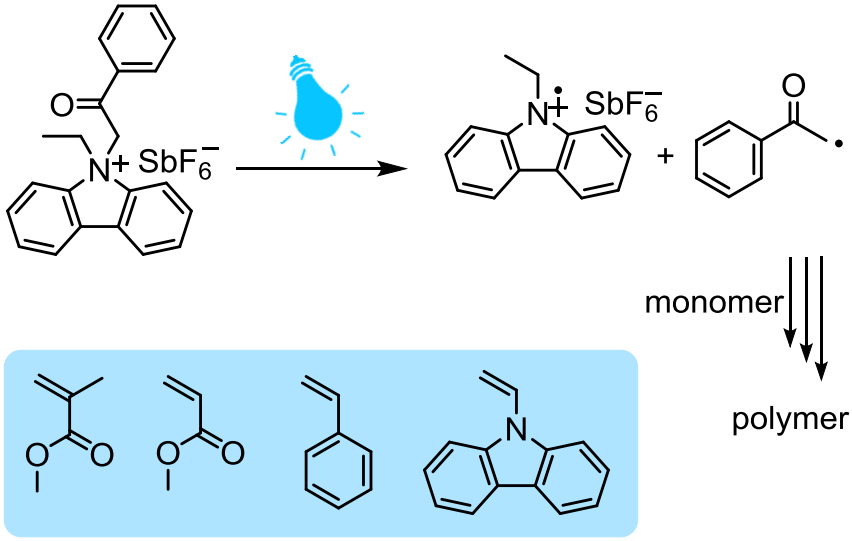


Figure 4.6 : Free radical photopolymerization of vinyl monomers using PECH photoinitiator under UV light irradiation.

4.4 Photoinitiated Cationic Polymerization

Cationic photopolymerization of cyclic monomers such as cyclohexene oxide and tetrahydrofuran as well as vinyl ethers such as isobutyl vinyl ether was also attempted using this photoinitiator.

In contrast to the general behavior of phenacyl-based photoinitiators in the photoinitiation of cationic polymerization, PECH failed to initiate the cationic polymerization of these monomers (Figure 4.7). This is probably due to the improbability of electron transfer to yield cationic species and PECH's tendency to couple through carbazole moieties. This assumption was further proved by cyclic voltammetry (CV) measurements.

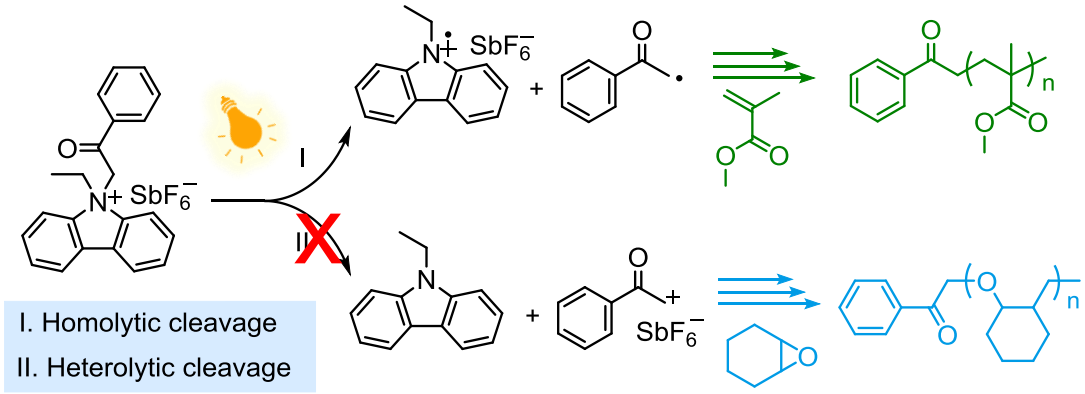


Figure 4.7 : Formation of radical and cationic species under UV light irradiation.

4.5 Photo-DSC Studies

Photo-DSC was used to study the kinetics of photocuring of bi-functional monomers. For this purpose, ethylene glycol dimethacrylate (EGDMA) was used in the presence of PECH as photoinitiator (Figure 4.8).

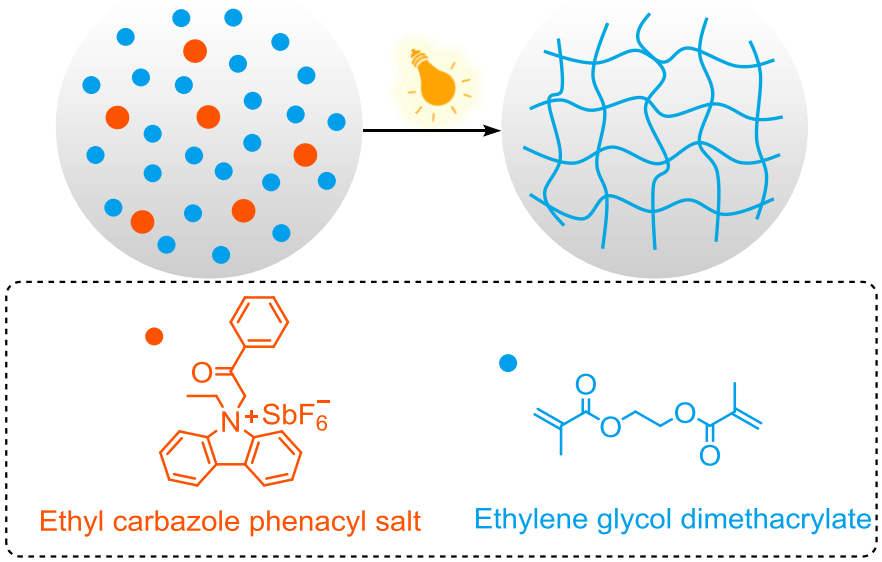


Figure 4.8 : Photoinitiated polymerization of ethylene glycol dimethacrylate in the presence of phenacyl ethyl carbazolium salt.

Photo-DSC, which is sensitive to any thermal changes due to the reaction of double bonds during the course of polymerization, gives a heat rate profile of polymerization by which the rate and real-time double bond conversion can then be calculated. Photocuring is rapidly achieved within less than 100 s reaching to above 35% double bond conversions. In order to compare the initiation efficiency of PECH photoinitiator, a typical *Type I* photoinitiator, namely 2,2-dimethoxy-2-

phenylacetophenone (DMPA), was used to conduct photocuring by means of photo-DSC. As can be seen from Figure 4.9, slightly higher efficiency observed with DMPA may be attributed to the higher reactivity of alkoxy benzyl radicals with electron donor substituents towards strong electron withdrawing monomers such as methacrylates [94]. Additionally, employing higher light intensities resulted in rapid photocuring processes. However, almost the same conversions were achieved in different light intensities (Figure 4.10).

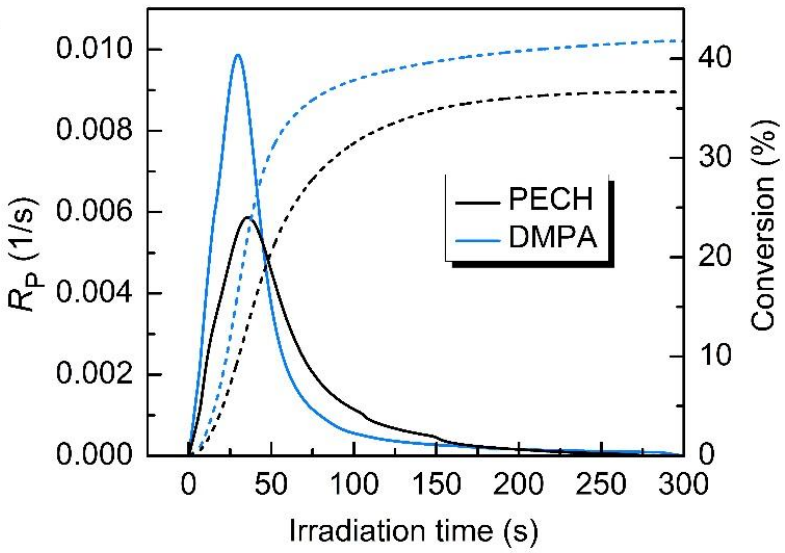


Figure 4.9 : Photocuring kinetics of EGDMA using PECH and DMPA as model photoinitiator obtained by photo-DSC (solid lines: rate of polymerization R_P(1/s) and dashed lines: double bond conversions (%)).

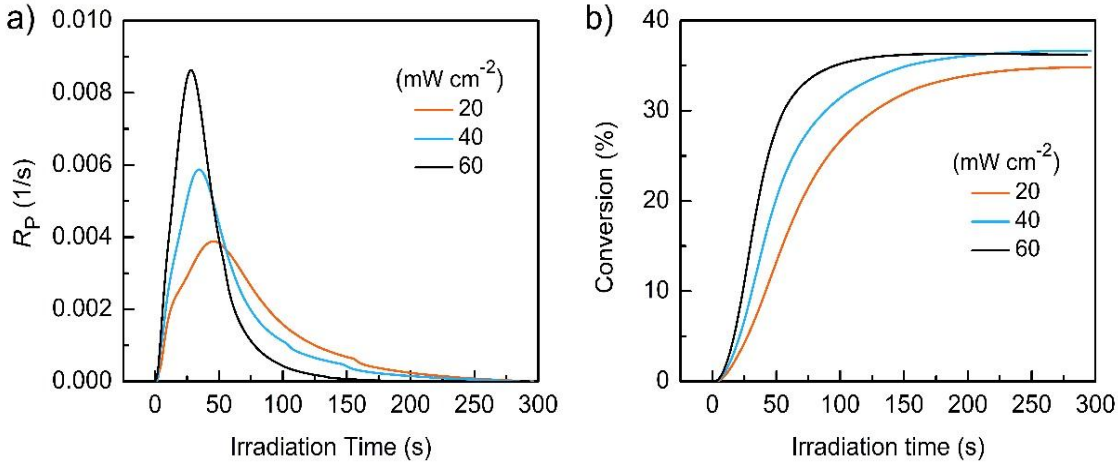


Figure 4.10 : Effect of various light intensities on photocuring kinetics of ethylene glycol dimethacrylate using phenacyl ethyl carbazolium hexafluoroantimonate measured by photo-DSC: a) rate of polymerization (1/s) and b) real-time double bond conversion (%).

4.6 CV Measurements

The initial reduction potential of the photoinitiator was found to be -1.41 V. This value is much negative compared to the reduction potential of the diphenyl iodonium salt (-0.2 V) and that of the alkoxy pyridinium salt (-0.7 V) which are known to undergo redox processes to generate cationic species [74, 95]. Figure 4.11 shows CV diagrams of the photoinitiator.

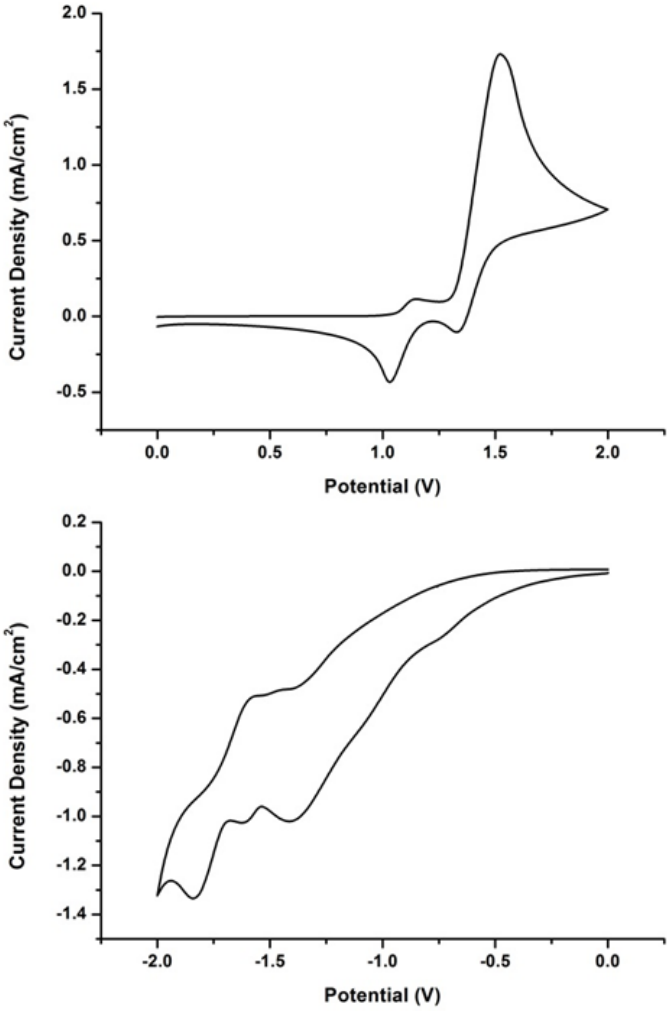


Figure 4.11 : Cyclic voltammetry diagrams of phenacyl ethyl carbazolium hexafluoroantimonate.

Thus, PECH does not initiate cationic polymerization through the electron transfer reactions of the photodecomposition products as would be expected on the basis of its reduction potential. Interestingly, during the CV measurements, a reversible color change indicating electrochromic behavior was observed. This observation is beyond the scope of the present work and requires detailed independent investigations.

5. CONCLUSION

In conclusion, a new phenacyl-based photoinitiator was synthesized and chracterized possessing conjugated ethyl carbazole moiety. The photoinitiator absorbs light at relatively higher wavelengths of the UV light. Free radical photopolymerization of a series of vinyl monomers including methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), and *N*-vinylcarbazole (NVC) was successfully achieved using this new photoinitiator. However, cationic photopolymerization of monomers including cyclic and vinyl ethers was failed. This may be due to the tendency of the photo-fragments to couple through carbazole units and thermodynamically unfavorable redox potential of the salt.

Further studies to gain insight into the electrochemical behavior of the salt are now in progress and will be reported elsewhere.

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PUBLICATIONS AND PRESENTATIONS ON THE THESIS:

- **Kara, M.,** Dadashi-Silab S., and Yagci Y., Phenacyl Ethyl Carbazolium as a Long Wavelength Photoinitiator for Free Radical Polymerization. *Macromolecular Rapid Communications*, 2015, DOI: 10.1002/marc.201500446.
- **Kara, M.,** Dadashi-Silab S., and Yagci Y., Fotobaşlatıcı Olarak Etil Karbazol-Fenaçil Tuzu: Sentezi ve Karakterizasyonu, *27. Ulusal Kimya Kongresi*, 2015, Çanakkale, Turkey. *(Poster presentation)*
- **Kara, M.,** Dadashi-Silab S., and Yagci Y., Synthesis and Characterization of Ethyl Carbazole-Phenacyl Salt as Photoinitiator for Free Radical Polymerization, *14th Bayreuth Polymer Symposium (BPS '15)*, 2015, Bayreuth, Germany. *(Poster presentation)*